

**DEVELOPMENT OF ANODIC ALUMINUM OXIDE  
TEMPLATES FOR GROWTH OF CuO NANORODS  
FOR PHOTODETECTION DIVICE**

**KHALED MAJID CHAHROUR**

**UNIVERSITI SAINS MALAYSIA**

**2016**

**DEVELOPMENT OF ANODIC ALUMINUM OXIDE  
TEMPLATES FOR GROWTH OF CuO NANORODS  
FOR PHOTODETECTION DEVICE**

by

**KHALED MAJID CHAHROUR**

**Thesis submitted in fulfillment of the requirements  
for the degree of  
Doctor of Philosophy**

**September 2016**

## **ACKNOWLEDGEMENT**

On this memorable day in my life, I reached the final destination of my PhD research study; first of all I bestowed the thanks to Allah Almighty for granting me health and patience with capability to complete this research work. I dedicate this thesis to the soul of my father, God have mercy on him. My heartfelt gratitude goes to all my family members for their continuous prayers, their support, and their encouragement. Words cannot sufficiently express how grateful I feel.

I would like to express my sincere thanks to my supervisor Dr. Naser Mahmoud Ahmed for his kind cooperation, useful contribution, and valuable guidance during my study and research work. I also wish to record my deep sense of gratitude to my co-supervisor Prof. Dr. Md Roslan Hashim for his useful and valuable suggestions, inspiring guidance, and consistent encouragement. He always taught me how to face hard moments in this research.

I acknowledge the Universiti Sains Malaysia (USM) Fellowship program for its financial support to this research. I express my gratitude as well to all staff members of the School of Physics, USM for their encouragement. To be fair I had to extend my sincere thanks to all of NOR laboratory staff for the cooperation and kindness behaviors with the all postgraduate students. I also thank all my friends and colleagues who supported me and helped me during the completion this thesis.

## **TABLE OF CONTENTS**

<b>ACKNOWLEDGEMENT</b>	<b>ii</b>
<b>TABLE OF CONTENTS</b>	<b>iii</b>
<b>LIST OF TABLES</b>	<b>ix</b>
<b>LIST OF FIGURES</b>	<b>x</b>
<b>LIST OF ABBREVIATIONS</b>	<b>xvii</b>
<b>LIST OF SYMBOLS</b>	<b>xix</b>
<b>ABSTRAK</b>	<b>xxi</b>
<b>ABSTRACT</b>	<b>xxiii</b>
<b>CHAPTER 1: INTRODUCTION</b>	
1.1 Introduction	1
1.2 Problem Statement	3
1.3 Research Objectives	3
1.4 Research Originality	4
1.5 Thesis Overview	5
<b>CHAPTER 2: LITERATURE REVIEW AND THEORETICAL BACKGROUND</b>	
2.1 Introduction	6
2.2 Types of Anodic Aluminum Oxide (AAO)	6
2.2.1 Nonporous Barrier-Type Oxide	6
2.2.2 Porous-Type Oxide	7

2.3	Pre-Treatment of Al Films	8
2.4	Mechanism of Pore Nucleation	9
2.5	Self- Organized Porous AAO Film	13
2.5.1	Two-Step Anodization	14
2.5.2	Structure Features of Self-Ordered Porous AAO Film	16
2.6	Modulation of the Pore Dimensions	19
2.6.1	Anodizing Voltage	19
2.6.2	Type and Concentration of the Electrolyte	21
2.6.3	Temperature Dependence	22
2.7	Syntheses of Functional Nanostructures Assisted by Porous AAO	23
2.7.1	Porous AAO Deposited onto Substrates	23
2.7.2	Removing Bottom Barrier Layer	24
2.7.3	Electrodeposition of Nanostructures Assisted by Porous AAO	26
2.8	Cupric oxide (CuO) nanostructures	30
2.8.1	Structural properties of CuO	30
2.8.2	Optical properties of CuO	31
2.9	Metal-Semiconductor-Metal Photodetectors	31
2.9.1	Metal-Semiconductor Contact	32
2.9.2	The Operational Parameters	33
2.8.2(a)	Current Gain	33
2.8.2(b)	Responsivity	34
2.8.2(c)	Quantum Efficiency	34
2.8.2(d)	Sensitivity	35
2.8.2(e)	Response Time and Recovery Time	35

2.9.3 The Photoconduction Mechanism	36
-------------------------------------	----

## **CHAPTER 3: EXPERIMENTAL PROCEDURE**

3.1 Introduction	39
3.2 Preparation of Substrates	39
3.2.1 Silicon Substrate	39
3.2.2 Glass Substrate	40
3.3 Radio Frequency (RF) Sputtering Technique	41
3.3.1 RF Sputtering of ITO onto Glass Substrates	41
3.3.2 RF Sputtering of Ti Interlayer onto Silicon and ITO-Glass Substrate	42
3.4 E- Beam Evaporation Technique	42
3.5 Thermal Annealing Furnace	44
3.6 Anodizing Experimental Setup	44
3.6.1 Horizontal Anodizing Cell	45
3.6.2 Vertical Anodizing Cell	47
3.7 Anodizing Processing	49
3.7.1 Current-Versus Time Anodization Characteristics	49
3.7.2 Two-Step Anodizing Process	50
3.7.3 Pore Widening	51
3.8 Direct Current Electrodeposition of Metal into AAO Template	52
3.9 Oxidizing Furnace	54
3.10 Chemical Etching for the Removal of AAO Template	55
3.11 Structural and Optical Instruments	56
3.11.1 Field Emission Electron Microscopy (FESEM) with EDX	56
3.11.2 Atomic Force Microscope (AFM)	59

3.11.3	High-Resolution of X-ray Diffractometer (HR-XRD)	60
3.11.4	Photoluminescence Spectroscopy (PL)	63
3.11.5	Raman Spectroscopy	64
3.11.6	UV-VIS-NIR Spectroscopy	66
3.12	Fabrication and Measurements of Devices	67
3.12.1	Fabrication of IR MSM Photodetector	68
3.12.2	Measurements of the Device	70
3.13	Summary	71
 <b>CHAPTER 4: FABRICATION OF THIN POROUS AAO TEMPLATES ON Si-SUBSTRATE AND ITO/GLASS SUBSTRATE</b>		
4.1	Introduction	72
4.2	Effect of the Annealing Time on Deposited Al Thin Films	73
4.2.1	Grain Size and Roughness of the Deposited Al Thin Film	73
4.2.2	Crystalline Structure of the Deposited Al Thin Film	75
4.3	Self-Organized of Thin Porous AAO Template by Using Two-Step Anodization	76
4.3.1	Study the Current Behavior as a Function of the Time during Anodizing Process	78
4.3.2	Microstructural Procedure of Fabrication Thin Porous AAO Template by Using Two-Step Anodization	81
4.4	Modulation of the Pore Dimensions of the Thin Porous AAO Template	83
4.4.1	Effect of the Anodizing Voltage	83
4.4.1(a)	Feature Parameters of Porous AAO Templates onto Si Substrate	83
4.4.1(b)	Feature Parameters of Porous AAO Templates onto ITO/Glass Substrate	89
4.4.2	Effect of the Anodizing Time	95

4.5	Effect the Wet Etching Time Cycles on the Morphology Features of Porous AAO Templates	99
4.5.1	Effect the Striping Cycles of the First-Step Anodization	99
4.5.2	Effect of Time on Pore Widening	100
4.6	Removal of the Bottom Barrier Layer	105
4.7	Structural Properties of AAO Template	106
4.8	Optical Properties of AAO Template	108
4.8.1	Transmittance of the AAO Template	108
4.8.2	Photoluminescence of the AAO Template	109
4.9	Summary	111

## **CHAPTER 5: GROWTH AND CHARACTERIZATION OF CuO NANOROD ARRAYS ONTO THIN POROUS AAO TEMPLATES AND FIBRICATION OF PHOTODETECTION DEVICE**

5.1	Introduction	113
5.2	Growth of Cu Nanorod Arrays into AAO Template by Direct Ccrrrent Electrodeposition	114
5.3	Structural Characteristics of the CuO Nanorod Arrays/AAO Assembly	116
5.3.1	Structural Analysis of Cu Nanorod Arrays	116
5.3.2	Structural Analysis of CuO Nanorod Arrays	119
5.3.3	Different Diameters of CuO Nanorod Arrays	121
5.4	Optimum Wet Etching Cycle of the Removing AAO Template	122
5.5	Raman Spectroscopy	125
5.6	Photoluminescence (PL) Spectroscopy of CuO Nanorod Arrays/AAO Assembly	126
5.7	Characteristics of the CuO Nanorod Arrays/AAO Assembly IR Photodetector Device	128
5.8	Characteristics of the CuO Nanorod Arrays IR Photodetector Device	134



5.9	Summary	141
<b>CHAPTER 6: CONCLUSIONS AND FUTURE WORKS</b>		
6.1	Conclusions	142
6.2	Future Research Works	144
	<b>REFERENCES</b>	145
	<b>APPENDICES</b>	161
	Appendix 1	161
	Appendix 2	163
	Appendix 3	165
<b>LIST OF PUBLICATIONS</b>		
	International journals	
	International conferences	

## LIST OF TABLES

	<b>Page</b>
Table 2-1    Controllable parameters: anodizing voltage, concentration and temperature of the electrolyte and structural features: interpore distance ( $D_i$ ), pore diameter ( $D_p$ ), pore wall thickness ( $W$ ), porosity and growth rate of self-organized porous AAO for sulfuric, oxalic and phosphoric acid [39].	18
Table 4-1    Structural features of porous AAO obtained by the two-step anodization of as-deposited Al thin film onto Si substrate in (0.3 M, 19 °C) oxalic acid at 35, 40, 45, 50 and 55 V, respectively and pore widening is 45 min.	89
Table 4-2    Structural features of porous AAO obtained by the two-step anodization of as-deposited Al thin film onto ITO/glass substrate in (0.3 M, 15 °C) oxalic acid at 40, 45 and 55 V, respectively and pore widening is 45 min.	93
Table 4-3    Mean of the thickness and aspect ratio of porous thin AAO film obtained by various times of the second-step anodization at 5, 10, 15, 20 and 25 min.	98
Table 5-1    Photodetection characteristics of the Al-CuO nanorod arrays/ AAO assembly-Al IR photodetector with increasing bias voltage.	133
Table 5-2    Photodetection characteristics of the Al-CuO nanorod arrays-Al IR photodetector with increasing bias voltage.	140

## LIST OF FIGURES

	<b>Page</b>
Figure 2.1 Two different types of anodic aluminum oxide (AAO) formed by (a) barrier-type and (b) porous-type anodizing process, along with the respective current density - time (j-t) transients under potentiostatic conditions [17].	8
Figure 2.2 Schematic of the pore nucleation mechanism in an acidic electrolyte [32].	11
Figure 2.3 Current-time transients during porous AAO formation showing the distinct pore growth stages [39].	13
Figure 2.4 Two-step anodization method: schematic drawings and corresponding SEM images for anodization in 0.3 M oxalic acid, anodizing voltage is 40 V, temperature of electrolyte at 4 °C. (a) Al foil surface as-rolled; (b) Al foil surface after standard pre-treatments; (c) top porous-alumina surface with random pore nucleation; (d) Al substrate top surface after chemical etching of the aluminum oxide formed during the first-step anodization, evidencing the patterned dimples; (e) top porous AAO surface after a second-step anodization [39].	15
Figure 2.5 Expansion of Al during anodic oxidation, depicting on the left the level of the unoxidized metal surface [2].	16
Figure 2.6 Schematic structure of (a) porous anodic aluminum oxide (AAO) on Al foil and (b) cross-sectional view [17].	17
Figure 2.7 Interpore spacing versus anodizing voltage. The known self-ordering regimes are shown as symbols. The line is a fit to the data with a proportional constant $k_i = 2.5$ nm/V. Experimental data extracted from Chu <i>et al.</i> [13] and Ono <i>et al.</i> [60].	20
Figure 2.8 (a, b and c) Top surface and (d, e and f) cross-section SEM image of porous AAO obtained with different anodizing parameters: [(a) and (d)] 0.3 M sulfuric acid, anodizing voltage is 25 V; [(b) and (e)] 0.3 M oxalic acid, anodizing voltage is 40 V; [(c) and (f)] 0.1 M phosphoric acid, anodizing voltage is 195 V [39].	22
Figure 2.9 Schematic picture of chemical etching of pore cell wall (a) hexagonal pore cell before pore widening, (b) pore cell wall become thinner and the pore size enlarged after pore widening, (c) pore cell wall become more thinner and the pore size more enlarged with increasing the pore widening time and (d) pore	

	cell wall begin to break in certain places and the remaining part in the sex corners formed alumina nanowires during exceed the pore widening time [109].	26
Figure 2.10	(a) Setup for the template-based growth of metallic NRs by potentiostatic, (b) the current density at different deposition stages when a constant voltage is applied [123, 139].	29
Figure 2.11	Formation of Schottky barrier between metal and p-type semiconductor: (a) neutral and electrically isolated, (b) in ideal contact [154].	33
Figure 2.12	Calculate of response time and recovery time from a pulse photocurrent.	35
Figure 2.13	The photoconducting mechanism in metal oxide such as (ZnO) nanowire: (a) Schematic of the metal oxide nanowire, (b) The nanowire in the dark with surrounding air, (c) The photogenerated electron-hole pairs as a result of photon illumination [162].	38
Figure 3.1	Experimental procedures flowchart.	40
Figure 3.2	(a) Image of the Auto HHV500 RF sputtering system (b) Schematic diagram of the RF sputtering.	41
Figure 3.3	(a) Image of the APX e-beam evaporator system (b) Schematic diagram of the e-beam evaporator (c) Sample-holder with four samples.	43
Figure 3.4	(a) Annealing tube furnace model Lenton VTF/12/60/700 (b) Schematic diagram of a thermal tube furnace.	44
Figure 3.5	Schematic diagram of horizontal anodizing cell set up.	46
Figure 3.6	Experimental setup of horizontal anodizing cell.	46
Figure 3.7	Schematic diagram of vertical anodizing cell setup.	48
Figure 3.8	Experimental setup of vertical anodizing cell.	48
Figure 3.9	Schematic diagram of experimental setup of I-t anodization.	49
Figure 3.10	Schematic diagram of two-step anodization.	51
Figure 3.11	Schematic diagram of pore widening.	52
Figure 3.12	Schematic diagram of DC electrochemical deposition.	53

Figure 3.13	Experimental setup of DC electrochemical deposition.	53
Figure 3.14	Linear sweep voltammogram for the cathodic reduction of copper solution.	54
Figure 3.15	(a) Oxidizing tube furnace model Nabertherm R701/9 (b) Schematic diagram of a thermal tube furnace.	55
Figure 3.16	Various emissions from the sample during the interaction of the electron beams with the sample.	57
Figure 3.17	A schematic of FESEM configuration.	58
Figure 3.18	Field emission scanning electron microscope and energy dispersive x-ray spectroscope.	59
Figure 3.19	(a) A schematic of atomic force microscopy (AFM) configuration (b) AFM system model Dimension edge, Bruker.	60
Figure 3.20	(a) Image of the high-resolution XRD equipment model PANalytical X pert PRO MRD PW 3040 (b) Schematic diagram of an x-ray diffraction experiment.	61
Figure 3.21	Bragg diffraction on a crystal. The angles at which diffraction occurs are a function of the distance between planes and X-ray wavelength.	63
Figure 3.22	PL instrument setup configuration.	64
Figure 3.23	Simplified Raman spectroscopy configuration.	65
Figure 3.24	Raman spectroscopy system model Jobin Yvon HR800UV.	66
Figure 3.25	(a) Schematic diagram of the spectrophotometer. (b) Image of Agilent Technologies Cary 5000 UV-Vis-NIR spectrophotometer.	67
Figure 3.26	Schematic image of finger shaped mask structure used in the fabrication of MSM photodetector.	68
Figure 3.27	Schematic diagram of Al-CuO nanorod arrays/AAO assembly-Al IR photodetector.	69
Figure 3.28	Schematic diagram of Al-CuO nanorod arrays-Al IR photodetector.	69
Figure 3.29	Experimental setup of the device's measurements.	70

Figure 4.1	FESEM images of Al thin film (a) as-deposited, (b & c) annealing at 500 °C for 2 h and 5 h, respectively.	74
Figure 4.2	AFM images of Al thin film (a) as-deposited, (b & c) annealing at 500 °C for 2 h and 5 h, respectively.	75
Figure 4.3	XRD pattern of Al thin film (a) as-deposited, (b & c) annealing at 500 °C for 2 h and 5 h, respectively.	76
Figure 4.4	FESEM images of AAO template made from thin Al film (a) top view and (b) cross-section of the AAO template of one-step anodization, (c) top view and (d) cross-section of the AAO template of two-step anodization under controllable parameters of anodizing process: anodizing voltage is 50 V, time of the second-step anodization is 20 min and pore-widening treatment for 45 min, (e) top view and (f) cross-section of Al concave pattern at the Al substrate top surface after stripping the AAO layer for 45 min.	77
Figure 4.5	Typical current-time transient recorded during first-step and second-step anodizing process.	79
Figure 4.6	The current-time curves during the period of porous AAO formation for three different voltages 40, 45 and 50 V. The upper inset shows the current transient recorded for 8 s during the anodizing process.	80
Figure 4.7	FESEM images (cross-sectional and top-view) (a) Al thin film after annealing, (b) porous AAO film after a first-step anodization, (c) wet-etching (stripping) of AAO film, (d) porous AAO film after a second-step anodization and (e) AAO film after pore widening at 45 min.	82
Figure 4.8	FESEM images show top-view of the porous AAO films. AAO films were prepared in (0.3 M, 19 °C) oxalic acid, under controllable parameter conditions: time of second-step anodization is 20 min and anodizing voltage 35, 40, 45, 50, 55 and 60 V, respectively. Pore widening time is 45 min.	84
Figure 4.9	Curve correlating (a) mean of pore diameter and (b) mean of interpore distance with voltage.	85
Figure 4.10	The dependence of (a) pore density and (b) porosity on anodizing voltage.	87
Figure 4.11	The dependence of porosity on anodizing voltage by utilizing image processor.	88

Figure 4.12	(a) FESEM images showing top-view of the porous AAO films. AAO films were prepared in (0.3 M, 15 °C) oxalic acid under controllable parameter conditions: time of second-step anodization is 20 min and anodizing voltage 40, 45 and 55 V, respectively. Pore widening time is 45 min. (b) EDX spectra.	90
Figure 4.13	Curve correlating (a) mean of pore diameter and (b) mean of interpore distance with anodizing voltage.	91
Figure 4.14	The dependence of (a) pore density and (b) porosity on anodizing voltage.	92
Figure 4.15	The dependence of porosity on anodizing voltage by utilizing image processor.	94
Figure 4.16	AFM images (a) Si-based AAO prepared under 40 V and (b) Si- based AAO prepared under 50 V.	95
Figure 4.17	FESEM images showing cross-section view of the porous AAO films. AAO films were prepared under controllable parameter conditions (0.3 M, 19 °C) oxalic acid and 40 V at various times of the second-step anodization 5, 10, 15, 20 and 25 min.	96
Figure 4.18	Thickness of the pore as a function of the time of second-step anodization.	97
Figure 4.19	Curve is correlating aspect ratio with a time of the second-step anodization.	98
Figure 4.20	FESEM images showing features of the AAO pore arrays after wet etching of the aluminum oxide layer of the first step of anodization (striping) for different time cycles (a) wet etching for 5 min, (b) wet etching for 20 min, (c) wet etching for 30 min and (d) wet etching for 45 min.	101
Figure 4.21	FESEM images showing the features of the AAO pore arrays were prepared in (0.3 M, 19 °C) oxalic acid and anodizing voltage is 50 V with pore- widening treatment for different times (a) pore widening for 20 min (b) pore-widening for 25 min, (c) pore-widening for 30 min and (d) pore-widening for 45 min.	102
Figure 4.22	AFM image of the AAO template prepared with pore-widening for 45 min.	103
Figure 4.23	(a, b) Curve correlating mean pore diameter and mean of pore cell wall thickness with pore-widening time, respectively. (c) FESEM image showing the pore nanostructure was destroyed when the pore-widening time was over 48 min.	104

Figure 4.24	(a, b) FESEM images showing the alumina nanowires will appear after breaking the hexagonal pore nanostructure of AAO.	105
Figure 4.25	FESEM images showing the cross-section view of AAO template, (a) without pore-widening and (b) pore-widening for 45 min at room temperature.	106
Figure 4.26	XRD patterns of porous AAO film (a) without annealing, (b) with annealing at 850 °C and (c) with annealing at 950 °C.	107
Figure 4.27	Transmittance of AAO template on ITO/Ti/glass.	108
Figure 4.28	Photoluminescence (PL) spectrum of AAO template (a) on Si substrate and (b) on ITO/glass substrate.	110
Figure 5.1	The current transient during the electrodeposition of the Cu into AAO template. (I) Nuclei forms on bottom of AAO template. (II) Cu atoms deposition around the pore. (III) The pores are filled with Cu nanorods to the top of AAO template. (IV) Hemispherical cap formation.	115
Figure 5.2	(a, b) FESEM image and AFM image show top view of the AAO template, (c, d) FESEM image shows a cross- section view of the AAO template and EDX spectra, respectively.	117
Figure 5.3	(a, b) FESEM image shows top view of Cu onto AAO template and EDX spectra, (c, d) FESEM image shows a cross-section view of Cu aligned nanorod arrays on Si substrate after removal of AAO template and EDX spectra, respectively.	118
Figure 5.4	XRD spectrum of Cu nanorod arrays embedded in AAO template.	119
Figure 5.5	(a, b) FESEM image shows cross-sectional of AAO template filled with Cu and EDX spectra, (c, d) FESEM image shows a cross-section view of CuO aligned nanorod arrays on Si substrate after thermal oxidation and EDX spectra, respectively.	120
Figure 5.6	XRD spectrum of CuO nanorod arrays embedded in AAO template.	121
Figure 5.7	FESEM images showing cross-section view of the CuO nanorod arrays standing onto Si substrate, (a) CuO nanorods with diameter around 50 nm, (b) CuO nanorods with diameter around 65 nm, (c) CuO nanorods with diameter around 75 nm, and (d) CuO nanorods with diameter around 110 nm, after removal the AAO templates had been anodizing at 35, 40, 45, and 55 V, respectively.	123



Figure 5.8	FESEM images show the cross-section view of CuO nanorods after removing the AAO template with different wet etching time cycles, (a) wet etching for 2 min, (b) wet etching for 7 min and (c) wet etching for 5 min.	124
Figure 5.9	Raman spectrum of CuO nanorod arrays embedded into AAO film.	125
Figure 5.10	Photoluminescence (PL) spectrum of CuO nanorod arrays embedded in AAO template.	127
Figure 5.11	Current-voltage characteristics of Al-CuO nanorod arrays/AAO assembly-Al photodetector (inset shows the logarithm of I-V characteristics) under dark and IR light (808 nm, 0.1 mW/cm <sup>2</sup> ).	129
Figure 5.12	Responsivity of the Al-CuO nanorod arrays/AAO assembly-Al photodetector under ambient conditions.	130
Figure 5.13	Repeatability performance of the Al-CuO nanorod arrays/AAO assembly -Al photodetector under on/off IR light (808 nm, 0.1 mW/cm <sup>2</sup> ) at different bias voltages.	132
Figure 5.14	Current-voltage characteristics of Al-CuO nanorod arrays/AAO assembly-Al photodetector (inset shows the logarithm of I-V characteristics) under dark and IR light (808 nm, 0.1 mW/cm <sup>2</sup> ).	134
Figure 5.15	Responsivity spectrum of the Al-CuO nanorod arrays-Al photodetector under ambient conditions.	136
Figure 5.16	Repeatability performance of the Al-CuO nanorod arrays-Al photodetector under on/off IR light (808 nm, 0.1 mW/cm <sup>2</sup> ) at zero bias voltage.	138
Figure 5.17	Repeatability performance of the Al-CuO nanorod arrays-Al photodetector under on/off IR light (808 nm, 0.1 mW/cm <sup>2</sup> ) at different bias voltages.	139

## LIST OF ABBREVIATIONS

a.u	Arbitrary unit
AAO	Anodic aluminum oxide
Ae <sup>-</sup>	Auger electrons
AFM	Atomic force microscope
Al	Aluminum
ALD	Atomic layer deposition
BSe <sup>-</sup>	Backscattering electrons
CCD	Charge coupled device
CE	Counter electrode
CNT	Carbon nanotubes
CuO	Cupric oxide
CV	Cyclic voltammetry
CVD	Chemical vapor deposition
DC	Direct current
DI	Deionized water
E- beam	Electron beam
EDX	Energy dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscopy
IR	Infrared
I-t	Current-time
ITO	Indium tin oxide
I-V	Current-voltage
LV	Linear voltammetry

MBE	Molecular beam epitaxial
MS	Metal-Semiconductor
MSM	Metal-Semiconductor-Metal
NBE	Near-band edge emission
NRs	Nanorods
NTs	Nanotubes
NWs	Nanowires
pH	Power of hydrogen
PD	Photodetector
PL	Photoluminescence
PLD	Pulsed laser deposition
RCA	Radio Corporation of America
RE	Reference electrode
RF	Radio frequency
RIE	Reactive ion etching
RMS	Root mean square
Se <sup>-</sup>	Secondary electrons
SPM	Scanning probe microscope
UV-VIS-NIR	Ultraviolet-Visible-Near infrared
WE	Working electrode
XRD	X-ray diffractometer

## LIST OF SYMBOLS

$A$	Active area
$c$	Speed of light in vacuum
$D_i$	Interpore distance
$D_p$	Pore diameter
$E$	Irradiance of the light
$E_c$	Conduction band
$E_{exc.}$	Excitation energy
$E_F$	Fermi level of semiconductor
$E_g$	Semiconductor band gap
$E_v$	Valance band
$h$	Plank's constant
$h, k, l$	Miller indices
$I_d$	Dark current
$I_{ph}$	Photocurrent
$k_p, k_i$	Proportionality constants
$n$	Order of reflection
$^{\circ}C$	Celsius temperature
$P$	Porosity
$P_{inc}$	Incident optical power
$q$	Electron charge
$R$	Responsivity
$R_p$	Growth rate of AAO film

$S$	Sensitivity
$V$	Voltage
$V$	Volume
$W$	Pore wall thickness
$\beta$	Barrier layer thickness
$\eta$	Quantum efficiency
$\theta$	Incident/Diffraction angle
$\lambda$	Wavelength
$\nu$	Frequency of light
$\rho$	Pore density
$\varphi_B$	Schottky barrier height
$\varphi_m$	Metal work function
$\varphi_s$	Semiconductor work function
$\chi$	Semiconductor electron affinity
$\tilde{\epsilon}$	Volume expansion
$a, b, c, \beta$	Lattice parameters

# **PEMBANGUNAN ACUAN ANOD ALUMINUM OKSIDA UNTUK PENUMBUHAN ROD NANO CuO DALAM PENGESANAN FOTO**

## **ABSTRAK**

Nanolang anod aluminium oksida (AAO) bertertib tinggi dan berbentuk heksagon berjaya ditumbuhkan daripada saput prapemendapan Al dengan ketebalan 1 $\mu$ m pada substrat Si dan ITO/kaca melalui penganodan dua-langkah. Mekanisme pertumbuhan saput liang AAO dikaji berdasarkan penganodan perlakuan arus-masa pada voltan yang berbeza, dan juga melalui pemerhatian mikrostruktur menggunakan keratan rentas dan pandangan atas daripada pengimejan (FESEM). Kajian mendapati liang dengan diameter (garis pusat) yang berjulat daripada 50 hingga 110 nm dan ketebalan di antara 250 dan 1400 nm, diperolehi dengan mengawal pengaruh dua parameter utama penganodan, iaitu voltan penganodan dan masa penganodan langkah kedua. Keadaan optimum pemboleh ubah proses seperti masa penyepuhlindapan bagi saput nipis Al yang termendak dan masa pelebaran liang daripada saput liang AAO ditentukan secara eksperimen bagi memperoleh saput AAO dengan mikrostruktur liang yang teragih secara seragam dan yang dijajar secara menegak. Pelebaran liang melalui rawatan punaran basar pada suhu bilik didapati mengubah kualiti liang saput AAO dan mengurangkan saput halangan bawah jajaran liang untuk memudahkan elektroenapan struktur nano ke atas saput AAO. Sebagai tambahan, permukaan Al yang cekung hemisfera memastikan bahawa pentertiban atau penyusunan sendiri liang AAO boleh diwujudkan apabila penjaluran digunakan selama 45 minit. Justeru, dapat dirumuskan bahawa tempoh rawatan punaran basar (penjaluran) pada saput Al oksida berlaku selepas

penganodan langkah pertama memainkan peranan penting dalam susunan terakhir nanoliang. Analisis belauan sinar-X menunjukkan transformasi fasa amorfus - kepada - hablur selepas penyepuhlindapan pada suhu melebihi 800°C. Imej AFM menunjukkan susunan optimum saput liang AAO teranod di bawah keadaan voltan yang rendah. Saput AAO boleh berfungsi sebagai templat dengan taburan saiz yang dikehendaki bagi fabrikasi jajaran nanorod CuO. Keputusan menunjukkan bahawa morfologi jajaran nanorod CuO yang dijajar amat terkesan oleh tempoh punaran basar dan penanggalan templat AAO. Kajian ini juga menunjukkan bahawa tempoh punaran basar optimum diperlukan untuk mengekalkan nanorod CuO dijajar tanpa sebarang fraktur adalah hampir 5 minit. Jajaran nanorod CuO prestasi tinggi /himpunan AAO dan pengesan foto IR susunan jajaran nanorod CuO yang berdiri bebas berdasarkan MSM difabrikasi dengan elektrod sentuhan-Al. Sambutan fotoelektrik dan elektrik dikaji, dan keputusan menunjukkan bahawa pengesan foto mempamerkan kepekaan yang tinggi terhadap diod laser infra merah (IR) 808 nm. Kedua-dua sambutan dan masa pemulihan didapati lebih cepat, iaitu masa yang lebih pendek dibandingkan dengan pengesan foto IR lain, yang dilaporkan dalam literatur.

# **DEVELOPMENT OF ANODIC ALUMINUM OXIDE TEMPLATES FOR GROWTH OF CuO NANORODS FOR PHOTODETECTION DEVICE**

## **ABSTRACT**

Ordered and hexagonal-shaped nanoporous anodic aluminum oxide (AAO) was successfully grown from 1  $\mu\text{m}$  thickness of Al pre-deposited onto Si and ITO/glass substrate using two-step anodization. The growth mechanism of the porous AAO film was investigated by anodization current-time behavior for different anodizing voltages and by microstructural observations using cross-sectional and top view of FESEM imaging. It was found that pores with diameter ranging from 50 to 110 nm and thicknesses between 250 and 1400 nm, were obtained by controlling two main influential anodization parameters: the anodizing voltage and time of the second-step anodization. The optimum conditions of the process variables such as annealing time of the as-deposited Al thin film and pore widening time of porous AAO film were experimentally determined to obtain AAO films with uniformly distributed and vertically aligned porous microstructure. Pore widening via wet-etching treatment at room temperature was found to modify the pore quality of AAO films and reduces the barrier layer on the bottom of AAO pore array facilitating a uniform electrodeposition of nanostructures onto AAO films. In addition, regular hemispherical concave Al surface ensuring the self-ordering of AAO pore can be established when striping is employed for 45 min. Thus, it could be inferred that the duration of wet etching treatment (striping) of Al oxide film performed after the first-step anodization plays a crucial role in the final arrangement of nanopores. X-ray diffraction analysis revealed amorphous-to-crystalline phase



transformation after annealing at temperatures above 800 °C. AFM images showed optimum ordering of the porous AAO films anodized under low voltage condition. AAO films could serve as templates with desired size distribution for the fabrication of CuO nanorod arrays. The results indicated that the morphology of the aligned arrays of CuO nanorods was strongly affected by the duration of etching and the removal of AAO template. This study showed also that the optimum etching duration required to maintain the aligned CuO nanorods without any fracture was approximately 5 min. High performance CuO nanorod arrays/AAO assembly and free-standing CuO nanorod arrays infrared (IR) metal-semiconductor-metal (MSM) photodetectors were fabricated with Al contact electrodes. The electrical performance and photoelectric response were studied and the results showed that IR photodetectors exhibited a high sensitivity to 808 nm IR laser diode. Both the response and recovery time were found to be fast; i.e. much shorter time compared to other IR photodetectors reported in the literature.

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Introduction**

Nanotechnology “the science that deals with nanometer-sized structures” is a fast-growing interdisciplinary field that extends exciting research in many fields, including physics, chemistry, material science and biology. Nanostructures exhibit unique physical and chemical properties due to quantum confinement effect compare to bulk counterparts. In recent years, many efforts have been focused on the development of expensive and inexpensive nanofabrication techniques. The large scale inexpensive fabrication methods remain one of the key mainstays of today’s nanotechnology. The search for such in low-cost fabrication alternatives, reaching the limits of current technologies, has led to a growing interest in nanoporous materials as templates for the controlled growth of nanostructures.

In particular, the porous anodic aluminum oxide (AAO) films formed by the electrochemical anodizing of aluminum have received significant attention in the synthetic nanostructure materials. The successful application of porous AAO as templates in many industrial fields, such as the manufacturing of nano-optoelectronic devices, is attributed to their highly controllable pore diameter and cylindrical shape, as well as periodicity and density distribution. In addition, AAO is electrically insulating, transparent and possessed high chemical and heat stabilities.

Previous studies have deduced that the most significant controllable parameters that influence the preparation of porous AAO films are the anodizing

voltage, type/concentration of the electrolyte, temperature and duration of anodization. For instance, by the controlling of the voltage during anodization, the possibility of modifying pore diameter as well as interpore distance increases exponentially. The thickness of the AAO films can also be modified by controlling the duration of anodization process.

Masuda and Fukuda [1] and Jessensky *et al.* [2] were the pioneers in describing how to fabricate an AAO template onto bulk Al foil with ordered hexagonal-shaped parallel nanotubes using a two-step anodization process. It has been reported that in order to obtain fully ordered nanotubes throughout the template, it is necessary to introduce a pre-arranged pattern before anodization. It was suggested that the anodization should be carried out in two steps. Most of the developed methods for producing self-organized AAO templates generally yield highly ordered arrays onto bulk Al foil. However, some challenges were encountered during the preparation of porous AAO templates of Al pre-deposited onto conducted substrates by using two-step anodization, including achieving highly-ordered porous AAO with open-through bottom barrier layer of pore structure.

In literature, different approaches have been used in the preparation of nanostructures into porous AAO template, such as chemical vapor deposition (CVD), physical vapor deposition (PVD) and electrochemical deposition. In the current research, the preparation of metallic nanostructures such as copper into porous AAO using electrochemical deposition, followed by thermal oxidation is the most promising and efficient method for the growth of vertically aligned cupric oxide nanorod arrays. The cupric oxide (CuO) has been a hot topic among the studies on transition metal oxides, because of its interesting properties as a p-type

semiconductor with a narrow band gap. The vertically aligned CuO nanorod arrays with large surface areas and size potential effect possesses superior physical and chemical properties. These significant CuO nanostructures have been extensively investigated, because of their promising applications in the photodetection devices.

## **1.2 Problem Statement**

During the two-step anodizing of Al thin film deposited onto substrate, due to the limited thickness of Al ( $\leq 1 \mu\text{m}$ ), the fabrication of uniform porous structure with vertically aligned nanotubes are not easily applicable. Also in the case of long time anodizing, which is known for producing well-ordered pore structure, the Al thin film can be easily detached from the substrate or develop cracks. These problems make the identification of optimum conditions to attain the required pore size, pore density and pore uniformity much more complex to be achieved in this research. Inability in optimizing the duration of pore widening prevents attaining high quality features of AAO pore arrays and obtaining homogeneous electrodeposition of nanostructures into AAO template. Nanorods fabricated using AAO are characterized by highly ordered and vertically well aligned nanostructures. However, the removal of AAO template causes the nanorods to collapse easily or aggregate into clusters due to their high surface tension. This has a negative influence on the fabrication of photodetection devices. Consequently, the control of the wet etching treatment procedure for the removal of AAO template has become imperative.

## **1.3 Research Objectives**

The main objectives of this research work can be summarized by the following points:

1. To synthesize highly-ordered thin AAO template onto Si and ITO/glass substrate, and study their growth parameters by controlling the intrinsic variables of anodization, including anodizing voltage and duration of the second-step anodization.
2. To develop a simple and efficient method to prepare uniform CuO nanorod arrays embedded into Si-based AAO template.
3. To study characteristics and performance of IR photodetectors based on aligned CuO nanorod arrays grown on Si substrate with or without AAO template.

#### **1.4 Research Originality**

The originality of this research work can be identified as follow:

1. Controllable pore-widening process by adjusting the pore diameter and removing the AAO bottom barrier layer at room temperature.
2. Microstructural procedure of the thin AAO film fabrication via two-step anodization has been visualized for the first time by using a cross-sectional FESEM imaging.
3. Elucidate a possible relationship between the morphology of aligned arrays of CuO nanorods during removal of AAO template and etching time, which has been reported for the first time.
4. No previous reports can be found in the literature so far about the fabrication of aligned CuO nanorod arrays IR metal-semiconductor-metal (MSM) photodetector by assisted AAO template.

5. Fabrication Al-CuO nanorod arrays-Al IR photodetector with ultra-fast response and recovery times at zero bias voltage.

## **1.5 Thesis Overview**

The content of this thesis is organized as follows: Chapter one contains a brief overview of an inexpensive and successful fabrication of the nanostructures by using self-organized porous AAO template, the main research problem, the research objectives and research originality. Chapter two presents a literature review and theoretical background of this study. Chapter three describes the principles of the experimental equipment, fabrication process and characterization instruments used in the preparation of porous AAO templates, growth of CuO nanorod arrays and for photodetection device applications. In chapter four, thin porous AAO films under controllable conditions of two-step anodization grown from pre-deposited Al thin film (1 $\mu$ m) thick onto Si and ITO/glass substrate are fabricated. The modulation of the AAO features (pore diameter and pore length) by modifying two controllable conditions (anodizing voltage and time of anodization) is involved in this chapter. In addition, this chapter explains the effect of the chemical wet etching time cycles (striping of the first-step anodization and pore widening) on the morphological features of Si-based AAO templates. The growth and characterization of CuO nanorod arrays into thin porous AAO template, as well as, fabrication and characterization of two MSM photodetector devices: Al-CuO nanorod arrays/AAO assembly-Al and Al-CuO nanorod arrays-Al are investigated in chapter five. Finally, conclusions and recommendations for future studies are reported in chapter six.

## **CHAPTER 2**

### **LITERATURE REVIEW AND THEORETICAL BACKGROUND**

#### **2.1 Introduction**

In this chapter, general fundamentals and basic theories of all required subjects involved in this research study are presented. It begins with classification of the AAO films into two categories according to their morphology. The advantage of heat treatment on Al films before anodization is clarified briefly. The mechanism of pore nucleation of the AAO is discussed. The procedure of self-organized of porous AAO by using two-step anodization is explained. The effect of anodizing parameters on modulation of the pore dimensions is reviewed. The growth of nanostructure materials by electrodeposition assisted porous AAO film also is reviewed. Moreover, the essentials of metal–semiconductor contacts and the basic principles of the metal-semiconductor-metal photodetectors are briefly described in this chapter.

#### **2.2 Types of Anodic Aluminum Oxide (AAO)**

Anodization of Al films in aqueous electrolytes produces anodic oxide films with two different morphologies, that is, the nonporous barrier-type oxide films and the porous-type oxide films. The different morphology depends on the chemical nature of the electrolyte [3-5].

##### **2.2.1 Nonporous Barrier-Type Oxide**

Barrier-type films are generally grown in an electrolytic cell with neutral electrolytes such as borate, oxalate, citrate, phosphate solution, etc. The grown film is insoluble in the electrolyte and consists of a thin compact layer of aluminum oxide

[6, 7]. Barrier-type oxide formation under potentiostatic conditions, current density ( $j$ ) decreases exponentially with time ( $t$ ). Correspondingly, the film growth rate decreases almost exponentially with time ( $t$ ), which points a limit on the maximum film thickness obtainable for barrier-type AAO films (Figure 2.1 (a)). It has been experimentally verified that the thickness of barrier-type film is directly proportional to the applied voltage.

### **2.2.2 Porous-Type Oxide**

Porous-type films are generally grown in an electrolytic cell with acidic electrolytes such as sulfuric [8], oxalic [9], phosphoric [10], chromic [11], malonic [12], tartaric [13], citric [14], squaric [15], malic acid [16] etc., in which anodic oxide is slightly soluble and consist of arrays of cylindrical shaped pores surrounded by an aluminum oxide structure.

Current density ( $j$ ) in porous-type anodization under potentiostatic conditions remains almost constant within a certain range of values during the anodization process, due to the constant thickness of the barrier layer at the pore bottom (Figure 2.1 (b)). The thickness of the resulting porous oxide film is linearly proportional to the total amount of charge (i.e., anodization time) involved in the electrochemical reaction. It has been experimentally verified that the thickness of porous-type film is directly proportional to the anodization time.



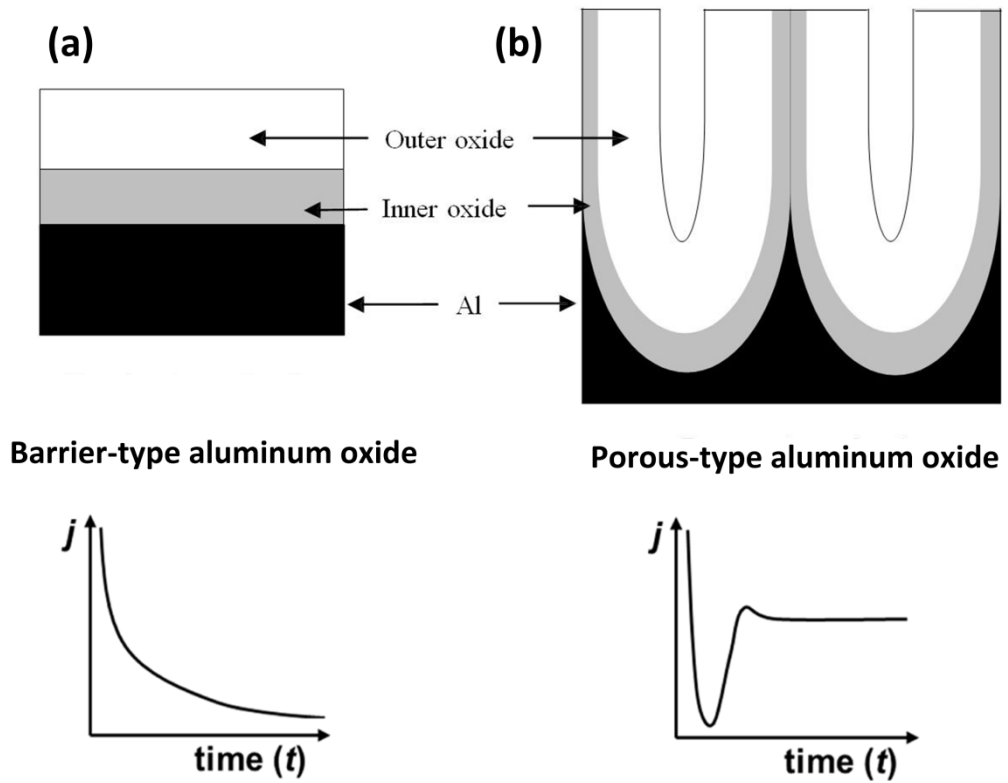


Figure 2.1 Two different types of anodic aluminum oxide (AAO) formed by (a) barrier-type and (b) porous-type anodizing process, along with the respective current density - time ( $j$ - $t$ ) transients under potentiostatic conditions [17].

### 2.3 Pre-Treatment of Al Films

The quality of the surface structure and/or the surface pre-treatments of the Al film will have a significant impact on the morphology and the nanoporous structures formed on the film surface during the anodizing process [18-21]. The purity of the Al film used has a direct impact on its dissolution rate in the acidic conditions of the electrolyte and thus, high purity Al is generally used. A purity of 99.99 % is commonly used. A typical pre-treatment of an Al film begins by first, degreasing the Al film using acetone or a similar solvent, then electrochemically polished in 1 M of sodium hydroxide solution for few minutes and finally washed in deionized water. This is followed by the annealing treatment; which is applied to the Al film to reduce

the mechanical stresses in the material and to modify the grain boundaries, since both these factors can have a significant effect on pore nucleation [22]. Annealing is usually performed at a temperature close to two-thirds of the melting point of Al usually between (400 - 500 °C) in an inert atmosphere, such as nitrogen or argon inside a conventional furnace [23]. The Al film is kept at this temperature for a suitable annealing period usually between (2 - 5 h) and then allowed to slowly cool in the inert atmosphere to prevent oxidation. During the annealing process the Al crystals reoriented to a preferred crystalline direction [24] and the Al grain size increases and the surface of the Al film becomes rougher and the larger grain boundaries can be observed [25, 26].

## **2.4 Mechanism of Pore Nucleation**

The origin of pore nuclei and the exact mechanism of pore nucleation are still clearly unknown. Several formation models have been proposed; one model explains that pore nucleation result from an electric field-assisted dissolution theory was first proposed by Hoar and Mott [27], but its effect on pore size, spacing and other porous AAO features were only presented in detail a few years later [28]. Thompson and Wood pioneered the understanding on the morphology, ion transport and initial stages of pore formation in porous AAO [29]. This model explains that pore nucleation results from an electric field assisted dissolution at the electrolyte/oxide interface and oxide generation at the metal/oxide interface.

In the early stages of the anodizing process,  $\text{Al}^{3+}$  ions migrate from the metal across the metal/oxide interface into the forming oxide layer. In the same time  $\text{O}^{2-}$  ions formed from water at the oxide/electrolyte interface travel into the oxide layer [30, 31]. During the oxide formation the barrier layer constantly regrows with further

oxide growth and transforms into a semi-spherical oxide layer of constant thickness that forms the pore bottom, as shown in Figure 2.2. During the formation of the porous oxide layer the anodic Al dissolution reaction is presented by



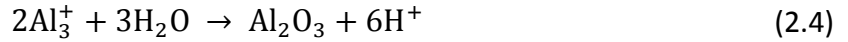
The resulting reaction at the cathode produces bubbles of hydrogen gas:



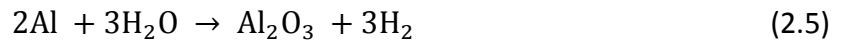
Anode reactions taking place at the metal/oxide interface (Oxygen anions react with Al)



At the oxide/electrolyte interface (Al cations react with the water molecules)



Overall reactions at electrode describe the simple reaction of anodizing process.



The steady state growth results from the equilibrium between the field-assisted oxide dissolution at the oxide/electrolyte interface at the base of the hemispherical shaped pores where the electric field is high enough to drive the  $\text{Al}^{3+}$  ions through the barrier layer and the oxide growth at the metal/oxide interface resulting from the migration of  $\text{O}^{2-}$  and  $\text{OH}^{-}$  ions into the pore base oxide layer.

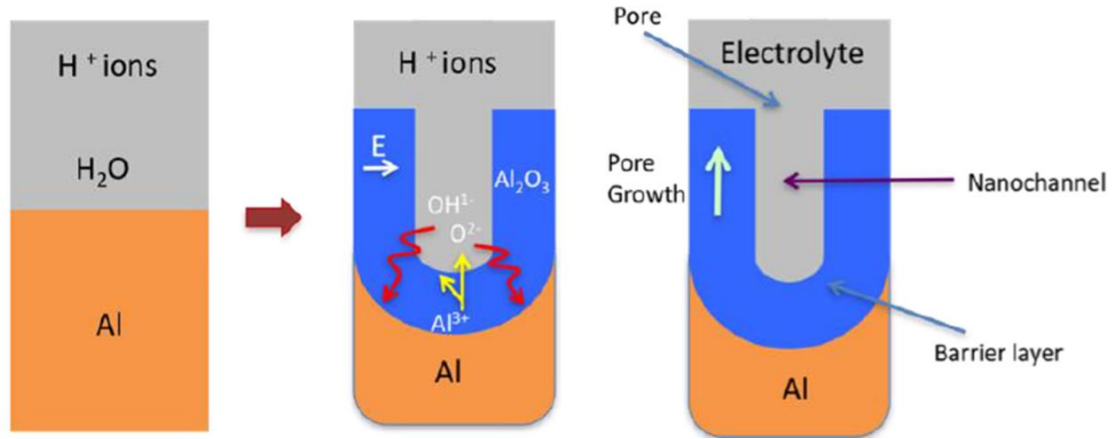


Figure 2.2 Schematic of the pore nucleation mechanism in an acidic electrolyte [32].

Shimizu *et al.* [33] described the initial pore formation process as a transition from a barrier-type film to a porous-type film, created by the cracking of the Al film under tensile stress, where the locally thinner sites become preferred sites for pore development. A theoretical model based on oxide growth at the metal/oxide and oxide/electrolyte interfaces and on field-assisted dissolution at the pore bottom, was then proposed by Parkhutik and Shershulsky [34]. Although a description of the porous AAO formation and growth was provided in this model.

Thamida and Chang [35] proposed a mathematical model accounted the effect of the surface curvature (roughness, perturbations) on converging the electric field at the troughs and diverging at the crests. Recently, a linear correlation between AAO pore depth and electric charge density during electrochemical anodizing process was determined and utilized to facilitate precise control of the porous AAO growth process in a wide range of voltage for a broad application [36].

In addition, the time dependence of the anodizing current during porous AAO formation is well established and can also provide insights into the growth process. Figure 2.3 shows a typical electric current curve monitored during the anodizing process where distinct regimes indicative of porous AAO structure formation can be identified [4, 25, 37, 38].

At first, the electric current decreases, it corresponding to the formation of barrier-type oxide film (regime (I)). Then, it passes through minimum value of electric current (regime (II)). Al is continuously oxidized and pore begin to grow in sites where irregularities on the surface topography. At these sites, the electric-field lines are converged, giving rise to localized heating due to electrical power dissipation. This effect results on enhanced chemical-assisted dissolution of the oxide. Subsequently, the electric current translates into a rise in value and it corresponds to the initial stage of pore nucleation and growth. In this stage numerous ionic conduction paths (pores) appear. Since some pores begin to stop growing due to competition among the pores, the current decreases again (regime (III)). Last, the electric current reaching a steady-state value (regime (IV)). The constant in electric current is indicative of equilibrium between oxide dissolution (at the electrolyte/oxide interface) and oxide growth (at the metal/oxide interface) giving a constant growth rate for the nanopores.

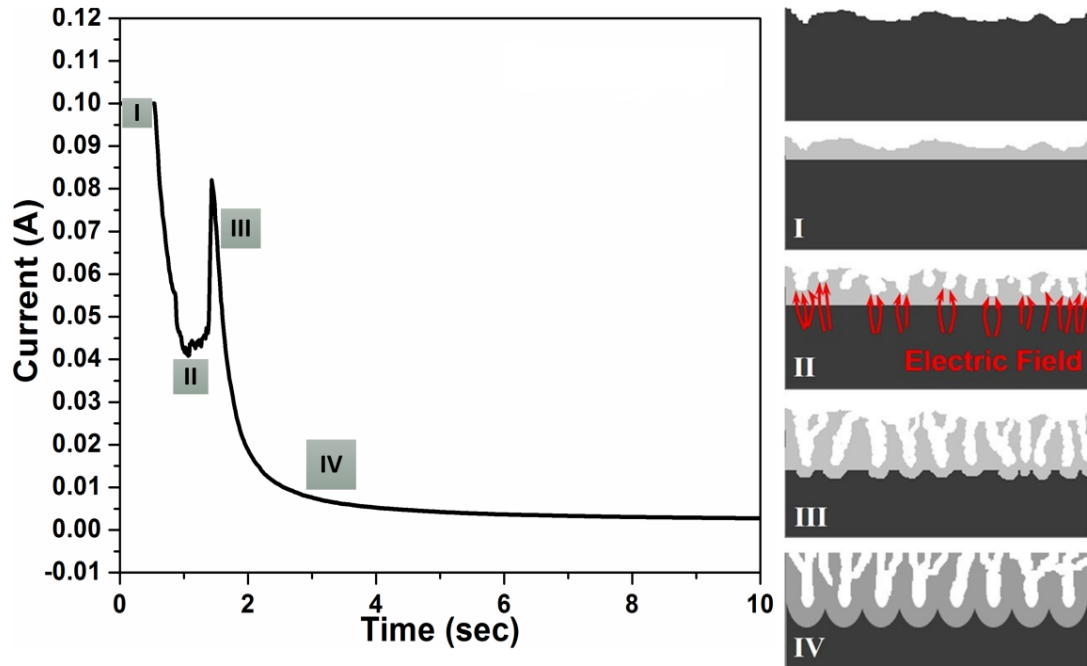


Figure 2.3 Current-time transients during porous AAO formation showing the distinct pore growth stages [39].

## 2.5 Self- Organized Porous AAO Film

Generally, there are two different techniques of porous AAO fabrication: a prepatterned-guided anodization resulting in a perfectly ordered nanopore arrangement and self-organized two-step anodization leading to a quasi-monodomain structure with partially areas of defects. The pre-patterning of Al film prior anodization can be carried out using a tip of the scanning probe microscope (SPM) [40, 41] and atomic force microscope (AFM) [42]. The patterning of Al film can be also formed by focused-ion beam lithography [43, 44]. Various molds with a regular array of convexes prepared lithographically have been also used for pre-patterning of Al film [45-47].

The main drawbacks of these pre-patterned anodization techniques are a time-consuming indentation of Al film before anodization and high-cost. Additionally, the perfect arrangement of nanopores of AAO is observed over the pre-patterned surface area of Al film only.

On the other hand, a self-organized two-step anodization of porous AAO can be carried out over a large surface area at the same time. The process of porous AAO formation by self-organized anodizing is simple, inexpensive and results in a high-density of nanopores but it is not free from defects in pore arrangement [37, 48, 49].

### **2.5.1 Two-Step Anodization**

Masuda and Fukuda, 1995 developed a two-step anodization method to obtain highly ordered porous AAO, without resorting to complex and costly lithographic techniques [1]. Their procedure involved two separated anodization processes onto bulk Al foil: a longer first anodization until order at the metal/ oxide interface is attained followed by oxide removal and a subsequent second-step anodization (Figure 2.4). While the first-step anodization at the original pre-treatment Al surface, the pores nucleated in (almost) random positions (Figure 2.4 (c)), ordered domain of Al dimples with area larger than 1  $\mu\text{m}$  are observed at the Al substrate top surface, after removing the porous aluminum oxide layer (Figure 2.4 (d)). During the second anodization, the pores will conveniently nucleate at the depressions of the Al surface, with the pattern guiding the nanopores growth. This leads to highly ordered hexagonal porous structures with domain of area larger than 1  $\mu\text{m}$ , depending on the first anodization time (Figure 2.4 (e)).

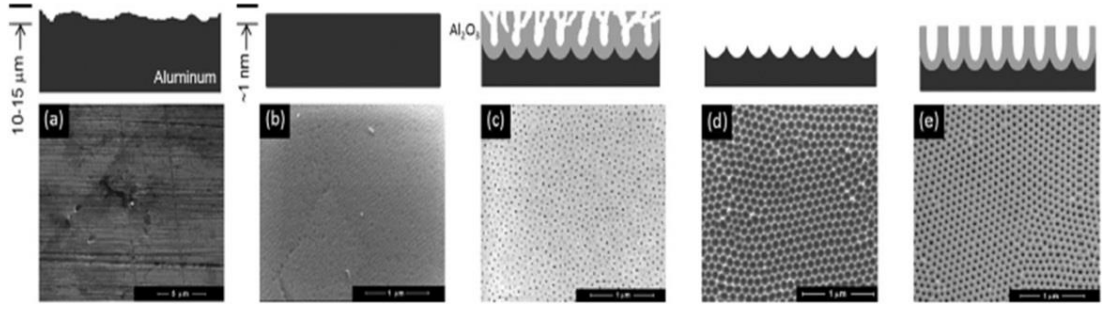


Figure 2.4 Two-step anodization method: schematic drawings and corresponding SEM images for anodization in 0.3 M oxalic acid, anodizing voltage is 40 V, temperature of electrolyte at 4 °C. (a) Al foil surface as-rolled; (b) Al foil surface after standard pre-treatments; (c) top porous-alumina surface with random pore nucleation; (d) Al substrate top surface after chemical etching of the aluminum oxide formed during the first-step anodization, evidencing the patterned dimples; (e) top porous AAO surface after a second-step anodization [39].

Many models pointed to slightly different mechanisms related to self-organized; one model explained the self-organized was a mechanical stress model proposed by Jessensky *et al.* [2, 50] based on repulsive forces between neighboring pores to explain the formation of hexagonally-ordered pore arrays. During the oxide growth at the metal/oxide interface, a volume expansion occurs (Figure 2.5) as a consequence of the lower atomic density that Al presents in  $\text{Al}_2\text{O}_3$  when compared to metallic Al. While the oxide is growing, the significant volume ( $V$ ) expansion ( $\check{\mathcal{V}} = V_{\text{Al}_2\text{O}_3}/V_{\text{Al}}$ ) leads to mechanical stress in the barrier-layer, expansion pore walls to grow only on the vertical direction and pushes the pore walls upwards [51].



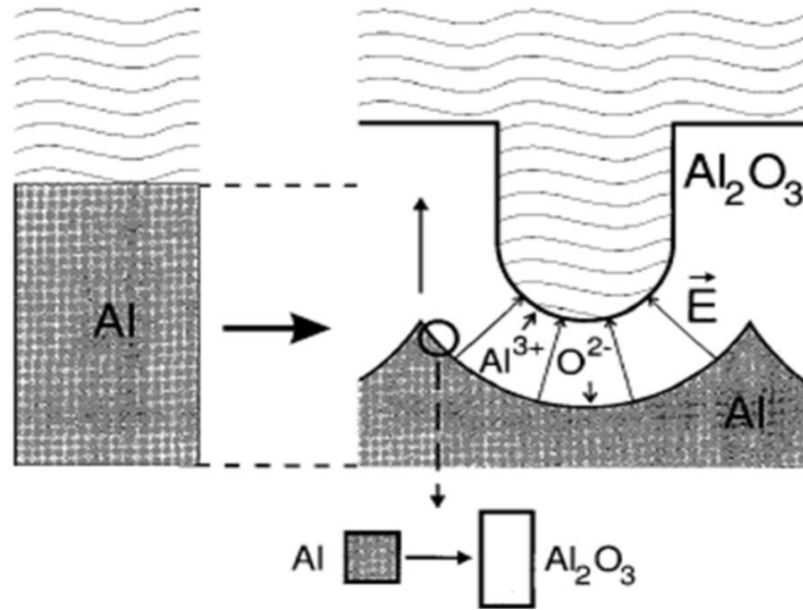


Figure 2.5 Expansion of Al during anodic oxidation, depicting on the left the level of the unoxidized metal surface [2].

However, not all oxidized Al gives rise to  $\text{Al}_2\text{O}_3$ , approximately 70% of the  $\text{Al}^{3+}$  ions and the  $\text{O}^{2-}$  ions contribute to the formation of the barrier oxide layer [30], the remaining  $\text{Al}^{3+}$  ions are dissolved into the electrolyte, and thus the real volume expansion was found to depend on anodizing voltage and electrolyte composition [52].

### 2.5.2 Structure Features of Self-Ordered Porous AAO Film

Figure 2.6 shows schematically an idealized structure of self-ordered porous AAO. Porous aluminum oxide layer formed on Al surface contains a large number of mutually parallel nanopores with honeycomb-like structure. Each circular nanopore consists of vertical pore channel and its surrounding aluminum oxide constitutes a hexagonal cell. The nanopore at the metal/oxide interface is closed by a thin barrier oxide layer with an approximately hemispherical morphology. The thickness of the

porous AAO layer on Al surface is easily tunable from a few tens of nanometers up to hundreds of micrometers by controlling the anodizing time [53].

In general, the structure of porous AAO is often defined by several structural features, such as interpore distance ( $D_i$ ), pore diameter ( $D_p$ ), barrier layer thickness ( $\beta$ ), pore wall thickness ( $W$ ), pore density ( $\rho$ ), defined as number of pores on the surface area of  $1 \text{ cm}^2$ , and porosity ( $P$ ), defined as a ratio of a surface area occupied by pores to the total surface area of oxide. Depending on experimental results, these structural features are mainly determined by anodizing parameters.

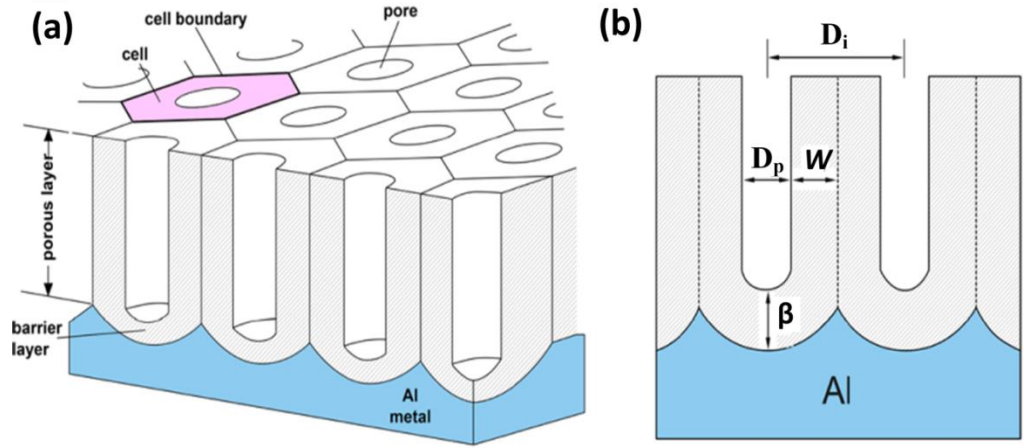


Figure 2.6 Schematic structure of (a) porous anodic aluminum oxide (AAO) on Al foil and (b) cross-sectional view [17].

For ideally ordered porous AAO, the different features can be calculated from the well-known Equations established for hexagonally arranged nanoporous structures [49]:

$$D_i = D_p + 2W \quad (\text{nm}) \quad (2.6)$$

Where,  $D_i$  is interpore distance,  $D_p$  is pore diameter and  $W$  is pore wall thickness.

$$\rho = \frac{2 \times 10^{14}}{\sqrt{3} \times D_i^2} \quad (\text{cm}^{-2}) \quad (2.7)$$

Where,  $\rho$  is the pore density and  $D_i$  is interpore distance.

$$p(\%) = \frac{\pi}{2\sqrt{3}} \times \left(\frac{D_p}{D_i}\right)^2 \quad (2.8)$$

Where,  $p$  is the porosity,  $D_p$  is pore diameter and  $D_i$  is interpore distance.

Highly-ordered hexagonal structures can be obtained of optimum parameters of anodizing process (Table 2.1), which samples exhibit a porosity  $P$  of  $\sim 10\%$ , and corresponding volume expansion  $\tilde{\epsilon} = 1.2$  [51]. In the case of sulfuric and phosphoric acid, the porosity for the optimum conditions is slightly higher than the expected 10 %, due to chemical etching of the aluminum oxide pore wall.

Table 2-1 Controllable parameters: anodizing voltage, concentration and temperature of the electrolyte and structural features: interpore distance ( $D_i$ ), pore diameter ( $D_p$ ), pore wall thickness ( $W$ ), porosity and growth rate of self-organized porous AAO for sulfuric, oxalic and phosphoric acid [39].

Acid	Sulfuric	Oxalic	Phosphoric
<b>Voltage (V)</b>	25	40	195
<b>Concentration (M)</b>	0.3	0.3	0.1
<b><math>D_i</math> (nm)</b>	65	105	480
<b><math>D_p</math> (nm)</b>	25	35	180
<b><math>W</math>(nm)</b>	$\sim 34$	$\sim 50$	$\sim 250$
<b>Porosity (%)</b>	$\sim 14$	$\sim 10$	$\sim 13$
<b>Growth rate (<math>\mu\text{m/h}</math>)</b>	5	2.5	5
<b>Temperature (<math>^{\circ}\text{C}</math>)</b>	$\sim 1$	$\sim 4$	$\sim 1$

## 2.6 Modulation of the Pore Dimensions

The controllable fabrication of thin porous AAO template under parameters conditions of anodizing process by using two-step anodization with tailoring the pore diameter, interpore spacing, thickness of thin porous AAO template through controllable of the critical parameters of anodizing process such as, anodizing voltage, concentration and electrolyte type and temperature are well-known effects [54-59].

### 2.6.1 Anodizing Voltage

The anodizing voltage,  $V$ , is one of the most important factors to adjust self-organized of porous AAO film. As shown in the Figure 2.7, the interpore distance ( $D_i$ ), is linearly proportional to the applied voltage with a proportionality constant  $k_i$  (nm/V) of approximately value is equal 2.5 for different types of acidic electrolyte [13, 52, 60].

$$D_i = k_i V = 2.5 V \quad (2.9)$$

In addition, large efforts have been made in the last years to widen the voltage vs.  $D_i$  range. Up-to-now, ordered porous AAO has been prepared in broad interval conditions as seen in the Figure 2.7 [39, 60, 61].

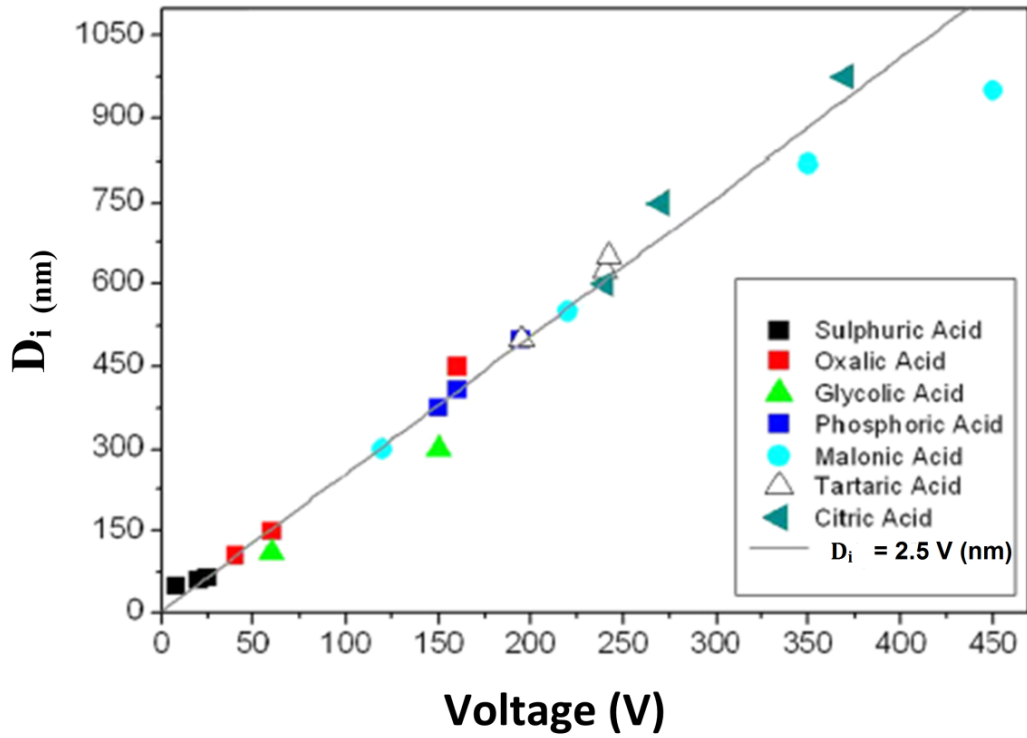


Figure 2.7 Interpore spacing versus anodizing voltage. The known self-ordering regimes are shown as symbols. The line is a fit to the data with a proportional constant  $k_i = 2.5 \text{ nm/V}$ . Experimental data extracted from Chu *et al.* [13] and Ono *et al.* [60].

The model proposed by O'Sullivan *et al.* [28] showed a linear relation between the pore diameter ( $D_p$ ) and the anodizing voltage. This relation was clarified by Xu *et al.* [62], which depends of the migration velocity of the reactive ions under the electric field during the growth and dissolution process of the forming porous AAO. This clarification was later supported by the study of Shingubara *et al.* [63] who investigated that voltage dependence on pore formation. A few years later, Lee *et al.* [64] reported that pore diameter ( $D_p$ ) increases with current density ( $j$ ) under potentiostatic anodization. Recently, many studies describe the fabrication of porous AAO with modulated of pore diameters by oscillatory current signals (anodization cyclic) [65].

Two other features (pore density and porosity) that characterize the porous AAO are related with the anodizing voltage. The pore density varies inversely as the square of the anodizing voltage [66]. Using 3 % oxalic acid, pore densities of the order  $10^{10}$  pores/cm<sup>2</sup> can be obtained. Pore densities ( $>10^{11}$  pores/cm<sup>2</sup>) can be obtained using 15 % sulphuric acid. Exponential dependence of pore density as a function of anodizing voltage was reported by Palibroda *et al.* [67]. In order to obtain perfect self-organized hexagonal arrays of nanopore formed during optimal anodizing parameters, the porosity of 10 % rule should be obeyed [51]. Recently, reports have published regarding changes in the porosity of porous AAO with increasing anodizing voltage [68, 69].

### **2.6.2 Type and Concentration of the Electrolyte**

The type and concentration of the electrolyte for a given anodizing voltage has to be selected properly to obtain self-ordered pore growth. In other words, the choice of the type of electrolyte is limited. Usually, the anodization of Al is carried out in sulfuric acid in low voltage range 5- 25 V, oxalic acid is used for medium voltage range 35- 80 V and phosphoric acid for high voltage range 80- 200 V. This limit is due to the conductivity and pH value of the electrolyte. For example, if Al is anodized in sulfuric acid at a high voltage (note that sulfuric acid has a very high conductivity), collapse of the porous AAO layer takes place very often. In addition, the pH-scale of the electrolyte determines the diameter of the pores. The lower the pH scale, the lower the voltage threshold for field-assisted dissolution at the pore boundary. This leads to a smaller size of the pores. Therefore, small pore diameters are formed by using the sulfuric acid, the medium pore diameters are formed by using the oxalic acid and the large pore diameters are obtained by using the

phosphoric acid [25]. Theoretical modeling of porous AAO growth performed by Parkutik and Shershulsky [34] predicted an increase in pore diameter with increasing pH electrolyte. (i.e., increasing electrolyte concentration) due to the enhanced dissolution velocity of anodic oxide at the pore base. Nielsch *et al.* [51] proposed the 10% porosity rule for the self-ordering regimes in three electrolytes such as sulfuric, oxalic, and phosphoric at anodizing voltages 25, 40, and 195 V, respectively as shown in Figure 2.8.

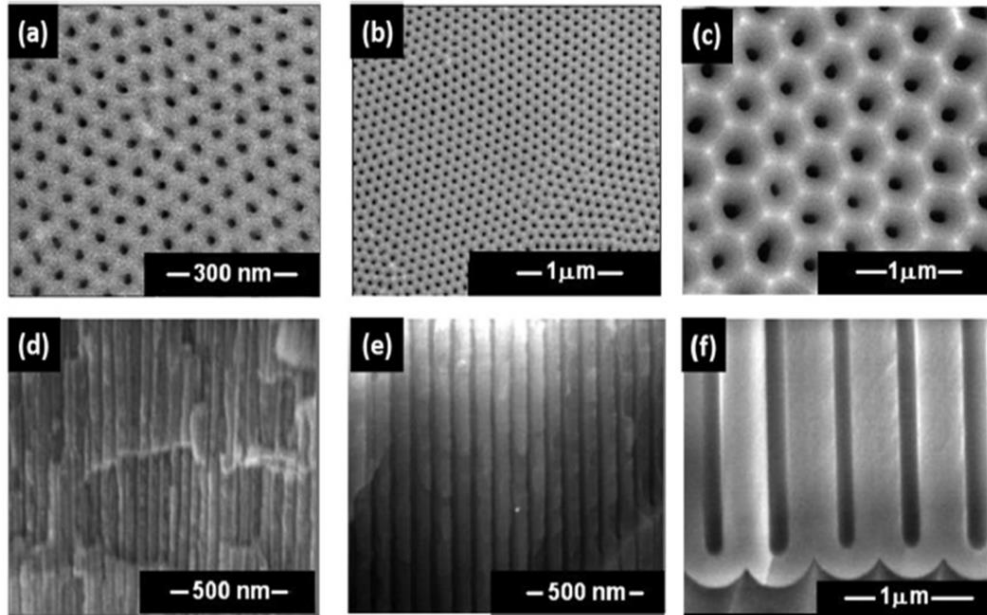


Figure 2.8 (a, b and c) Top surface and (d, e and f) cross-section SEM image of porous AAO obtained with different anodizing parameters: [(a) and (d)] 0.3 M sulfuric acid, anodizing voltage is 25 V; [(b) and (e)] 0.3 M oxalic acid, anodizing voltage is 40 V; [(c) and (f)] 0.1 M phosphoric acid, anodizing voltage is 195 V [39].

### 2.6.3 Temperature Dependence

During the anodizing process, temperature should be kept lower than room temperature to prevent the formed oxide structure from being dissolved in acidic

electrolytes. For instant, anodization at 40 V in oxalic acid is performed at 5- 19 °C and in the case of anodization at 195 V in phosphoric acid is performed at 0- 2 °C. Additional reason to keep the temperature as low as possible is to avoid a local heating at the bottom of the pores during the period of anodization (specially, the anodizing process at a high voltage). The local heat causes an inhomogeneous electric field distribution at the bottom, leading to local electrical collapse of the oxide layer. Recently study by Sulka and Parkoła indicated that the pore diameter increases with increasing temperature [58]. During the anodizing process, the electrolyte should be vigorously stirred to efficiently remove local heat and hydrogen bubbles on the Al surface, and to allow a homogenous diffusion of anions into pore channels [70].

## **2.7 Syntheses of Functional Nanostructures Assisted by Porous AAO**

Synthesis of functional nanostructures into porous AAO template provides many unique opportunities, allowing simple and cost-effective preparations of extended high-ordered arrays of nanostructures and also overcoming many of drawbacks of conventional state of the art lithographic techniques.

### **2.7.1 Porous AAO Deposited onto Substrates**

There are two major kinds of porous AAO, the first- type of porous AAO is grown on a bulk pure Al foil while the second- type is grown on conductive or metal-coated substrates. The second- type of the porous AAO is preferable. In addition to overcoming the brittle characteristics of porous AAO originated from Al bulk after removal the Al backing, porous AAO grown onto thin Al film ( $> 1 \mu\text{m}$ ) deposited on conductive or metal-coated substrates would potentially offer much broader



application than those on bulk Al foils [71, 72]. The substrate could be semiconductor such as Si [73-78], non-valve metal (e.g., Cu, Ag, Au, Pt, etc.)-coated Si substrates [72, 79-82], valve-metal (e.g., Ti, W, Ta, etc.)-coated Si substrates [83-85] and transparent indium tin oxide (ITO) [86-89].

Most of the developed methods for producing porous AAO generally yield highly ordered arrays on bulk Al foil. Until now, the fabrication of highly ordered thin porous AAO on substrates is difficult to be formed mainly due to the complicated surface states (roughness and crystallite sizes) and non-uniformity of the deposited Al film [71, 87] and still remains a major challenge from the scientific and technological point of view [90]. Moreover, the degree of pore ordering remains relatively not highly, even if a two-step anodization process is used, because of the limited thickness ( $\leq 1 \mu\text{m}$ ) of the Al film [88].

Porous AAO formed by anodizing thin Al films on substrates have been successfully utilized not only as patterning masks, but also as templates for fabricating various functional nanostructures (nanotubes, nanorods, nanowires and nanodots), including ordered arrays of metal [71, 91-93], semiconductor [84, 94-96], carbon nanotubes (CNT) [97-99], or polymer [100, 101] on various substrates.

### **2.7.2 Removing Bottom Barrier Layer**

Despite the broad range of potential applications of Si-based or ITO/glass-based AAO film, the prevalent problem is the barrier layer formed at the bottom of the AAO pores, which inhibits direct physical and electrical interaction with the substrate. Hence, diverse techniques have been employed to remove the bottom barrier layer such as, pore widening [72, 102], cathodic polarization [74, 103], voltage drop [104, 105] and reactive ion etching (RIE) [106, 107].